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Contributions to the Mineral Chemistry of Hawaiian Rocks. VI. Olivines in Rocks from Haleakala and West Maui Volcanoes, Maui, Hawaii[1]

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ABSTRACT: Phenocryst and groundmass olivine in 22 rocks of the tholeiitic, alkalic, and nephelinic suites from Haleakala and West Maui volcanoes were analyzed by electron microprobe. Results and conclusions: Ranges for average compositions of olivine phenocrysts and groundmass are, respectively, Fo_{73-85} and Fo_{61} for the tholeiitic suite (only one tholeiite contained groundmass olivine); Fo_{54-83} and Fo_{15-68} for the alkalic suite; and Fo_{73-83} and Fo_{61-66} for the nephelinic suite. In all suites, zoning extends these ranges substantially. Phenocrysts are usually enriched in Fe, Mn, and Ca at their rims, and coexisting groundmass olivine is richer in these same elements and depleted in Cr and Ni contents. In the differentiated alkalic suite, Fe, Mn, and Ca increase, and Ni decreases, from basalt to trachyte (mainly dependent on major element fractionation). The tholeiitic and nephelinic suites can occasionally be distinguished by higher Ca and lower Ni in olivine of the latter.

Keil et al. (1972) and Fodor et al. (1975) published compositional studies of feldspar and pyroxene in 24 rocks of the tholeiitic, alkalic, and nephelinic suites from Haleakala and West Maui volcanoes, Maui, Hawaii. The study of the mineral phases in these volcanic rocks was begun in an effort to understand the origin and history of these rocks, especially in regard to the genetic relationships between the three suites, and as a means of classifying basaltic volcanic rocks on the basis of mineral composition. In this paper, analyses of phenocryst and groundmass olivine in 22 of the same 24 rocks are reported (for a description of the samples, their localities, and bulk chemical characteristics, see Keil et al. 1972).

Major and minor element concentrations in olivines of volcanic rocks have previously been discussed by, for example, Simkin and Smith (1970), Boone and Fernandez (1971), and Stephenson (1974). However, studies of olivine composition from one major basaltic volcanic source as related to changing magma types (with time), including a highly differentiated suite, has not previously been carried out. The analytical results presented here will be used to attempt classification of rock types according to olivine composition and to determine the geochemical factors responsible for varying olivine compositions, particularly as related to changes in the bulk rock chemistry.

METHOD OF STUDY

Polished thin sections of the tholeiitic, alkalic, and nephelinic rocks were studied

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TABLE 1

AVERAGE COMPOSITIONS (IN WT %) AND COMPOSITIONAL RANGES FOR OLIVINE PHENOCRYSTS (p) AND GROUNDMASS OLIVINE (g) FROM ROCKS OF THE THOLEIITIC SUITE, HALEAKALA AND WEST MAUI VOLCANOES, MAUI, HAWAII

	C-100	C-121	C-123		C-120
	p	p	p	g	p
SiO_2	39.5	38.8	40.0	36.4	38.0
Cr_2O_3	0.05	0.05	0.09	0.05	0.03
FeO	18.5 (17.8–19.2)	20.8 (19.1–31.0)	14.4 (9.8–29.5)	33.7 (28.9–37.6)	24.2 (15.6–29.4)
MnO	0.24	0.23	0.15	0.42	0.28
MgO	42.0 (40.8–42.8)	40.0 (31.4–41.0)	45.2 (32.1–49.0)	29.6 (33.5–26.7)	37.1 (32.9–44.6)
CaO	0.28 (0.11–0.37)	0.30 (0.05–0.47)	0.22 (0.13–0.39)	0.34 (0.19–0.55)	0.20 (0.05–0.33)
NiO	0.22	0.14	0.39	0.17	0.19
Total	100.79	100.32	100.45	100.68	100.0
Fa	19.8	22.6	15.2	39.0	26.8
Fo	80.2 (79.1–81.1)	77.4 (64.4–79.3)	84.8 (66.0–89.9)	61.0 (56.0–67.4)	73.2 (66.6–83.6)

NOTE: Averages of 50 to 100 microprobe analyses each. For Mg/Mg + Fe ranges, also see Figure 1.

microscopically, and analyses of olivine were made with an ARL-EMX-SM electron microprobe. An olivine (Fo_{85}) similar in composition to many of the olivines analyzed served as a standard for Fe and Mg, a high-Ca pyroxene was used for Ca and Mn, a pure Ni for Ni, and chromite for Cr. Amount of SiO_2 was calculated stoichiometrically, and MgO was determined from a curve made from microprobe analyses of wet-chemically analyzed olivines. Analytical precision is about 1 percent of the amounts present for major elements and about 5 percent for elements in concentrations less than 1 wt %. In samples where phenocryst and groundmass olivine were abundant, 50 to 100 electron microprobe point analyses were made on each size category and averaged. However, for groundmass olivine compositions, averages based on 50 point analyses are more common.

RESULTS

Tholeiitic Suite

Only four of six tholeiitic samples contain olivine and only one contains groundmass olivine (in keeping with the definition of tholeiitic basalts, where little or no olivine is present). Average forsterite contents for the phenocrysts range from 73 to 85 mole %, with normal zoning near grain edges extending the compositional range from 64 mole % to 90 mole % (Table 1, Figure 1); an increase in Mn is usually associated with the increase in Fe at grain rims. Groundmass olivine in C-123 is greatly enriched in Fe and Mn, slightly enriched in Ca, and depleted in NiO relative to coexisting phenocrysts (Table 1). Amounts of Cr_2O_3 present in phenocrysts were <0.10 wt %. The concentrations for FeO, MnO, and NiO in olivine (Table 1) are similar to those measured in olivines of other tholeiitic basalts, such as at Makaopuhi lava lake, Hawaii (Moore and Evans 1967), east Molokai, Hawaii (Beeson 1976), and Thingmuli, Iceland (Carmichael 1967).

Alkalic Suite

The alkalic suite (basalt, hawaiite, mugearite, trachyte) displays a wide range in olivine composition, largely because of two highly differentiated samples, trachytes C-92 and C-116. Average forsterite contents in the phenocrysts of the most mafic members of this suite range between 74 and 83 mole %, although normal zoning, which in most cases occurs close to rims, extends this range from

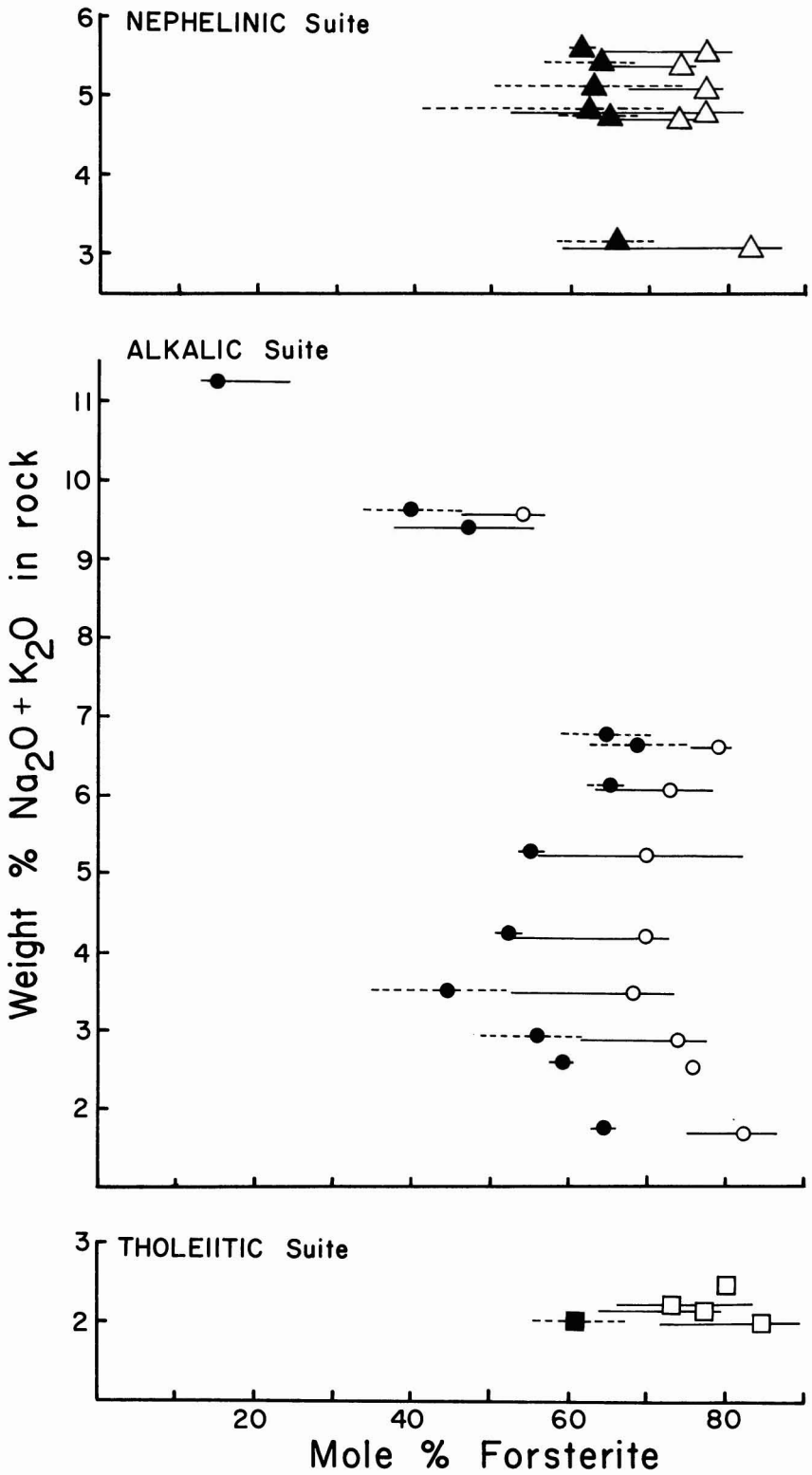

FIGURE 1. Mole percent forsterite (Fo, Mg_2SiO_4) in olivine plotted against bulk-rock total alkali contents for the tholeiitic, alkalic, and nephelinic suites. Open symbols, phenocrysts; closed symbols, groundmass; lines and dashes indicate compositional ranges.

62 mole % to 87 mole % (Table 2, Figure 1). Similarly, samples of hawaiite have olivine phenocrysts nearly as high in forsterite contents (average, Fo_{68-79}). Groundmass olivine in all the basaltic rocks and hawaiites are enriched in Fe relative to coexisting phenocrysts (average, Fo_{68-45}) (Table 2, Figure 1). In the one mugearite, groundmass olivine is Fe-rich (Fo_{38-56}), and in the trachytes, C-92 and C-116, olivine phenocrysts average Fo_{59} and the groundmasses are Fo_{40} and Fo_{15}, respectively. In most cases where phenocrysts coexist with groundmass olivine, there is compositional overlap (Figure 1); the absence of overlap may indicate olivine crystals that are actually xenocrysts which crystallized elsewhere (e.g., C-118 is transitional to an ankaramite). The presence of olivine in the groundmass of alkalic basalts C-125 and C-126 is notable because these rocks were previously (Keil et al. 1972, Fodor et al. 1975) considered transitional to tholeiitic basalt; here, the presence of olivine is compatible with their classification as alkalic.

In the hawaiites, the elements Mn and Ca increase at grain margins along with Fe; similarly, Mn and Ca are enriched in groundmass olivine relative to phenocrysts (Table 1). The Cr_2O_3 contents are below the detection limit except for small concentrations (<0.05 wt %) in olivine of the mafic members of the alkalic suite. In some samples, NiO is present in phenocrysts at concentrations of <0.10 wt %, and is slightly less in coexisting groundmass olivine.

Nephelinic Suite

Olivine phenocrysts in the six nephelinic samples have average compositions restricted to 73 mole % to 83 mole % forsterite, but zoning near the rims of phenocrysts reaches Fo_{59} (Table 3, Figure 1). Similarly, average compositions for groundmass olivine are limited to Fo_{61-66}, but zoning in one sample extends to Fo_{40}. Concentrations of the minor elements Mn and Ca are higher in the groundmass olivine than in the phenocrysts, and there is commonly an increase in Mn and Ca with increasing Fe near the rims of phenocrysts.

DISCUSSION

Crystallization Trends

The observed olivines richest in Mg are in the range of Fo_{80-90} and are not characteristic of any particular rock unit, as indicated by the presence of such olivine compositions in each of the three suites (Figure 1). Similar forsterite values have been reported for tholeiitic volcanic rocks of Hawaii by Moore and Evans (1967), Evans and Wright (1972), and Beeson (1976). More commonly, olivine phenocrysts in the mafic rocks of Maui have average compositions between Fo_{70-80}, and groundmass olivines are Fo_{50-70} (Figure 1). In the differentiated alkalic suite, olivine in a mugearite and two trachytes are greatly enriched in fayalite content relative to olivine in alkalic and alkalic olivine–basalt and hawaiite. Phenocrysts in members of the tholeiitic and nephelinic suites have no significant within-suite differences in Mg/Mg+Fe ratios (Figure 1).

The trend of Fe enrichment in olivines of the alkalic suite (Figure 1) is a function of changing magma composition during differentiation; higher fayalite (Fa) content is favored in differentiated magmas. Although the tholeiitic and nephelinic suites are not differentiated, increasing fayalite content in olivine with differentiation in these suites would also be expected, as indicated by examination of olivines in other provinces (e.g., Thingmuli, Iceland, Carmichael 1967; South Qoroq, Greenland, Stephenson 1974). In the volcanic rocks of Maui, the increase in Fe content in olivine from one rock to another was attended by an increase in Fe in coexisting high-Ca pyroxene, as shown in Figure 2*A*. This is particularly notable for the highly differentiated alkalic suite and reflects the general increase in bulk-rock total FeO/MgO ratio throughout differentiation from basalt to trachyte (Macdonald and Katsura 1964, Macdonald and Powers 1968).

The geochemical affinity of Mn for Fe is apparent in Figure 2*B*, where MnO in olivine increases with decreasing Fo content (increasing Fe). Like Fe enrichment, Mn enrichment is a function of bulk-magma composition and

TABLE 2

AVERAGE COMPOSITIONS (IN wt %) AND COMPOSITIONAL RANGES FOR OLIVINE PHENOCRYSTS (p) AND GROUNDMASS OLIVINE (g) FROM ROCKS OF THE ALKALIC SUITE, HALEAKALA AND WEST MAUI VOLCANOES, MAUI, HAWAII.

	C-118		C-125		C-126	
	p	g	p	g	p	g
SiO_2	39.7	36.8	38.9	36.5	39.4	36.0
Cr_2O_3	0.04	0.03	0.05	0.05	0.04	0.03
FeO	16.3 (12.6–22.4)	30.6 (29.5–32.3)	22.0 (21.6–22.3)	34.7 (33.8–35.9)	23.4 (20.3–33.0)	37.1 (34.0–42.0)
MnO	0.22	0.53	0.25	0.44	0.28	0.43
MgO	43.6 (39.0–46.6)	31.5 (32.5–31.0)	39.2 (38.7–39.6)	28.6 (27.4–29.0)	38.0 (30.2–40.0)	26.7 (23.0–29.1)
CaO	0.27 (0.12–0.53)	0.28 (0.17–0.45)	0.29 (0.18–0.42)	0.37 (0.20–0.49)	0.30 (0.19–0.46)	0.32 (0.21–0.47)
NiO	0.21	0.16	0.12	0.04	0.18	0.10
Total	100.34	99.9	100.81	100.7	101.6	100.68
Fa	17.3	35.3	23.9	40.5	25.7	43.8
Fo	82.7 (75.6–86.6)	64.7 (63.1–66.3)	76.1 (75.6–76.6)	59.5 (57.6–60.5)	74.3 (62.0–77.8)	56.2 (49.4–60.5)

	C-143		C-147		C-146
	p	g	p	g	g
SiO_2	39.2	37.1	37.8	36.9	36.9
Cr_2O_3	0.01	0.01	0.01	0.01	0.01
FeO	19.2 (18.0–22.0)	27.4 (22.3–31.2)	24.3 (19.6–31.1)	30.0 (28.4–31.6)	30.3 (26.5–34.1)
MnO	0.25	0.63	0.37	0.68	0.76
MgO	41.2 (38.7–42.0)	33.7 (29.7–38.3)	36.6 (30.6–40.2)	32.0 (30.8–33.0)	31.5 (28.5–35.0)
CaO	0.32 (0.20–0.46)	0.41 (0.28–0.58)	0.28 (0.15–0.47)	0.47 (0.29–0.72)	0.47 (0.35–0.61)
NiO	0.07	0.01	0.01	0.01	0.01
Total	100.25	99.26	99.37	100.07	99.95
Fa	20.7	31.3	27.1	34.5	35.0
Fo	79.3 (75.8–80.6)	68.7 (62.9–75.4)	72.9 (63.7–78.5)	65.5 (63.5–67.4)	65.0 (59.8–70.2)

NOTE: Averages of 50 to 100 microprobe analyses each. For Mg/Mg + Fe ranges, also see Figure 1.

TABLE 2 (*Cont.*)

	C-124		C-140		C-137	
	p	g	p	g	p	g
SiO_2	37.6	34.1	37.8	35.4	37.8	35.7
Cr_2O_3	0.03	0.03	0.01	0.01	0.03	0.03
FeO	28.0 (23.5–36.8)	45.2 (42.6–50.6)	26.8 (24.7–39.4)	39.3 (37.8–40.1)	26.7 (16.3–36.5)	37.6 (35.8–38.3)
MnO	0.40	0.87	0.35	0.78	0.44	0.88
MgO	34.1 (27.0–37.0)	19.5 (17.3–21.0)	35.0 (23.6–37.3)	24.5 (23.4–25.2)	35.2 (26.8–42.8)	26.0 (25.5–27.0)
CaO	0.35 (0.20–0.46)	0.37 (0.17–0.57)	0.37 (0.31–0.49)	0.46 (0.29–0.62)	0.30 (0.17–0.52)	0.49 (0.32–0.52)
NiO	0.07	0.05	0.09	0.08	0.10	0.07
Total	100.55	100.12	100.42	100.53	100.57	100.77
Fa	31.5	56.5	30.0	47.4	29.9	44.8
Fo	68.5 (56.7–73.7)	43.5 (37.9–46.8)	70.0 (51.6–72.9)	52.6 (51.0–54.3)	70.1 (56.7–82.4)	55.2 (54.3–57.9)

	C-141		C-92		C-116
	p	g	p	g	g
SiO_2	35.9	34.6	35.6	33.6	30.8
Cr_2O_3	0.01	0.01	0.01	0.01	0.01
FeO	33.6 (32.0–35.8)	42.5 (37.1–48.2)	38.2 (36.0–42.3)	46.5 (43.1–50.0)	57.9 (53.0–58.8)
MnO	0.90	1.5	1.5	2.2	4.5
MgO	28.4 (26.0–29.9)	21.3 (16.5–26.2)	25.3 (21.5–26.7)	17.4 (14.3–19.7)	5.8 (5.0–10.1)
CaO	0.36 (0.22–0.47)	0.71 (0.48–0.88)	0.19 (0.10–0.39)	0.61 (0.45–0.78)	0.77 (0.43–0.95)
NiO	0.04	<0.01	<0.01	<0.01	<0.01
Total	99.21	100.62	100.80	100.32	99.78
Fa	39.9	52.8	45.9	60.0	84.8
Fo	60.1 (56.4–62.5)	47.2 (37.9–55.7)	54.1 (47.5–56.9)	40.0 (33.8–44.4)	15.2 (13.2–25.3)

TABLE 3

AVERAGE COMPOSITIONS (IN WT %) AND COMPOSITIONAL RANGES FOR OLIVINE PHENOCRYSTS (p) AND GROUNDMASS OLIVINE (g) FROM ROCKS OF THE NEPHELINIC SUITE, HALEAKALA AND WEST MAUI VOLCANOES, MAUI, HAWAII

	C-130		C-135		C-142	
	p	g	p	g	p	g
SiO_2	40.2	37.0	38.9	36.9	38.5	37.0
Cr_2O_3	0.05	0.05	0.01	0.01	0.01	0.01
FeO	16.1 (12.7–34.7)	29.6 (26.2–33.9)	21.0 (18.9–28.8)	31.9 (22.9–37.4)	23.9 (21.7–31.8)	30.8 (27.9–35.1)
MnO	0.19	0.48	0.39	0.85	0.35	0.69
MgO	43.2 (27.5–46.2)	32.0 (29.6–34.8)	39.6 (33.0–39.8)	30.4 (22.9–37.4)	37.5 (30.9–39.1)	31.5 (27.7–34.0)
CaO	0.24 (0.10–0.44)	0.74 (0.57–0.91)	0.34 (0.24–0.48)	0.60 (0.37–0.82)	0.25 (0.14–0.35)	0.33 (0.23–0.56)
NiO	0.11	0.05	0.06	0.01	0.01	0.01
Total	100.09	99.92	100.3	100.67	100.52	100.34
Fa	17.3	34.2	22.9	37.1	26.3	35.4
Fo	82.7 (58.6–86.6)	65.8 (60.9–70.3)	77.1 (67.1–79.0)	62.9 (52.2–74.4)	73.7 (63.4–76.3)	64.6 (58.0–68.5)

	C-139		C-136		C-148	
	p	g	p	g	p	g
SiO_2	38.5	36.9	38.3	37.0	38.8	36.6
Cr_2O_3	0.01	0.01	0.01	0.01	0.02	0.02
FeO	20.7 (18.0–31.4)	32.9 (31.3–33.2)	23.8 (22.5–31.9)	31.4 (28.5–37.0)	21.0 (17.1–39.3)	32.3 (24.1–47.4)
MnO	0.29	0.62	0.39	0.66	0.29	0.52
MgO	39.2 (30.2–41.2)	29.2 (28.7–30.6)	37.6 (30.6–38.2)	31.0 (26.5–33.1)	39.5 (24.3–42.7)	30.0 (18.0–36.3)
CaO	0.41 (0.30–0.63)	0.70 (0.60–1.0)	0.36 (0.25–0.49)	0.46 (0.29–0.70)	0.37 (0.17–0.58)	0.60 (0.35–0.83)
NiO	0.09	0.05	0.01	0.01	0.10	0.06
Total	99.2	100.38	100.47	100.54	100.08	100.1
Fa	22.9	38.7	26.2	36.2	23.0	37.7
Fo	77.1 (63.2–80.3)	61.3 (60.6–63.5)	73.8 (63.1–75.2)	63.8 (56.1–67.4)	77.0 (52.4–81.7)	62.3 (40.4–72.9)

NOTE: Averages of 50 to 100 microprobe analyses each. For Mg/Mg + Fe ranges, also see Figure 1.

major element fractionation (Simkin and Smith 1970), and is most apparent in the differentiated alkalic suite.

A relationship between Ca and Fe is also present in the differentiated alkalic suite (Figure 2*C*), where there is a weak trend showing Ca increasing with Fe; like Mn, Ca is partly dependent on major element fractionation. High Ca in Fe-rich olivine is expected over Mg-rich olivine because Fe $\rightleftarrows$ Ca is theoretically more extensive than Mg $\rightleftarrows$ Ca (Warner and Luth 1973). This is also clear from relationships between coexisting phenocrysts and groundmass olivine, where greater amounts of Ca are found in the relatively Fe-rich groundmass olivine (Tables 1–3).

The Ni content in olivine is directly related to Mg content and decreases systematically with decreasing Mg. This trend, based on major-element fractionation, is particularly notable in the differentiated alkalic suite (Figure 2*D*); as stated by Forbes and Banno (1966), olivine of "primitive basalts" have comparatively higher Ni content than olivine of more highly differentiated basalts. The same applies to Cr, which is low in overall concentration, but nevertheless higher in olivine having high Mg contents (Tables 1–3).

Relationships of NiO between coexisting phenocryst and groundmass olivine favor a greater concentration in the phenocrysts. This is the opposite of what Beeson (1976) reported for olivine in basaltic rocks from Molokai, Hawaii. He proposed that greater Ni concentration in groundmass olivine relative to phenocrysts was a function of pressure. But he suggests that the absence of his observed relationship may be caused by other compositional variations of lavas.

Rock Suites Based on Olivine Composition

Mafic members of the tholeiitic, alkalic, and nephelinic suites cannot be distinguished on the basis of Mg/Mg+Fe ratios in olivine (Figure 1). Only the differentiated samples (mugearite, trachyte) within the alkalic suite can be separated from the most mafic members by the low Mg/Mg+Fe ratios in olivine of the differentiated rocks. Similarly, MnO content in olivine is not diagnostic in the mafic members of any suite, but in olivine of the differentiated alkalic suite, MnO is high. In general, Mn performs the same role as Fe in distinguishing rock types according to olivine compositions (i.e., highest in differentiated rocks; Figure 2*B*). In a study of olivines, however, Simkin and Smith (1970) observed some highly undersaturated (nephelinic) rocks to have olivine relatively high in Mn even at the forsterite-rich compositional end.

To separate the least alkalic from the most alkalic rock suites, Ni and Ca may be used. Tables 1 and 3 and Figure 2 show that for olivines having similar Fo contents ($\sim$70 to 80 percent), higher NiO contents are present in olivine of the tholeiitic suite. Low NiO in olivine of undersaturated rocks was previously noted by Simkin and Smith (1970). Because olivine is the only phase of basaltic magmas that concentrates significant amounts of Ni, the olivine analyses presumably reflect higher Ni concentrations in tholeiitic versus highly alkalic basaltic magmas. This is difficult to document in the literature, however. In fact, the opposite may be true, as indicated by Prinz (1967). But a comparison of Ni values in nephelinic rocks of Oahu (Nockolds and Allen 1954) to Ni in saturated rocks of Molokai, Hawaii (Beeson 1976), shows that many tholeiitic rocks have high-bulk Ni contents (e.g., 0.03 wt % to 0.05 wt % NiO).

Higher CaO content in phenocrysts and groundmass olivine vaguely separates the nephelinic suite from the tholeiitic suite and the mafic members of the alkalic suite (Figure 2). High CaO in olivine of undersaturated lavas has previously been discussed by Simkin and Smith (1970) and Stormer (1973), who demonstrated a general relationship between the bulk-rock SiO_2 saturation and the CaO content of the olivine.

Stormer (1973) calculated that Ca content in olivine, $Ca(SiO_4)_{\frac{1}{2}}$, should be sensitive to variation of silica activity of the liquid. This was also reported by Keil et al. (1972) and Fodor et al. (1975) to account for the higher CaO content in feldspar and pyroxene, respectively, in nephelinic rocks of Maui

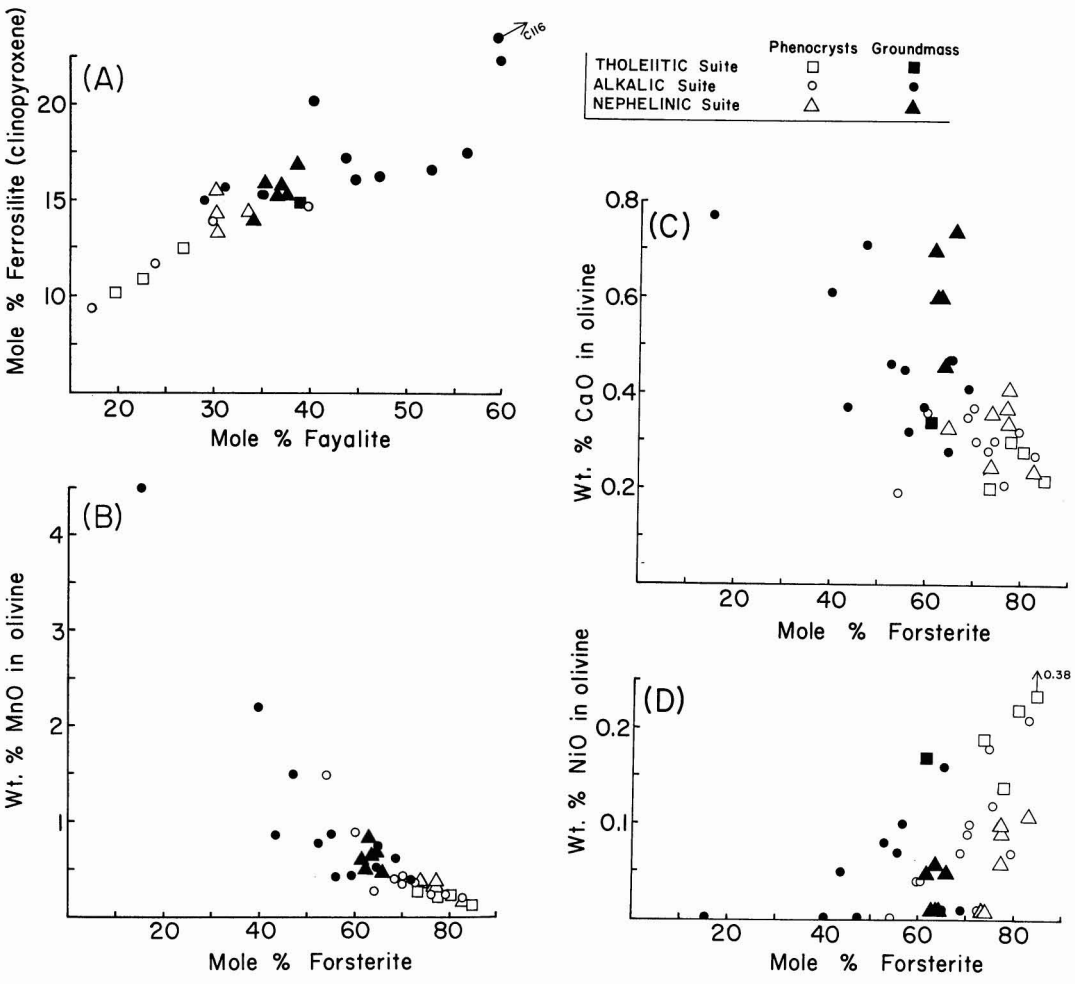

FIGURE 2. *A*, Mole percent fayalite (Fa, Fe_2SiO_4) versus mole percent ferrosilite (Fs, $FeSiO_3$) for olivine and high-Ca pyroxene, respectively, coexisting in the same rock (C-116 plots at Fs 30; Fa 85). *B*, Mole percent Fo (Mg_2SiO_4) plotted against weight percent MnO in olivine. *C*, Mole percent Fo plotted against weight percent CaO in olivine. *D*, Mole percent Fo plotted against weight percent NiO in olivine.

compared to tholeiitic and alkalic rocks. That is, the lower silica activity in the nephelinic rocks favored $CaAl_2Si_2O_8$ in feldspar and $CaAl_2SiO_6$ in pyroxene. Similarly, the relatively low silica-activity in the nephelinic rocks favors $Ca(SiO_4)_{\frac{1}{2}}$ in precipitating olivines. Experimental data of Warner and Luth (1973) show that higher pressure favors decreasing solubility of $CaMgSiO_4$ in olivine, but these data are largely for olivine coexisting with monticellite. Because nephelinic magmas are probably derived from higher-pressure regimes than are tholeiitic and alkalic magmas (e.g., Kushiro 1975, Ringwood 1975), olivine phenocrysts in nephelinic magmas may have crystallized under greater pressure than olivine in tholeiitic or alkalic magmas. Then, if a pressure effect does decrease Ca solubility in olivine (even in monticellite-free magmas), it is apparently compensated and offset by the more important influence that silica activity has on Ca entering olivine, as indicated by the slightly higher CaO generally observed in olivine of nephelinic rocks.

The increase in Ca (along with Mn and Fe)

at the rims of some phenocrysts in alkalic and nephelinic samples may have been due to a response to a sudden drop in pressure as the magma ascended and erupted (Stormer 1972, 1973), but the enrichment of Fe at grain margins also suggests the action of Ca:Fe exchanges.

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